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THE LASL THERMOCHEMICAL HYDROGEN
PROGRAM STATUS ON OCTOBER 31, 1978*

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The LASL program in thermochemical hydrogen can conveniently be thought of in four sections that are listed below:

- . Fusion Synfuel (Hydrogen) Project
- . Experimental research in support of cycles under development and funding from DOE/STOR
- . The International Energy Agency (IEA) Agreement on Thermochemical Hydrogen, Annexes I and II
- . Cycle Evaluation - DOE Thermochemical Cycle Evaluation Panel
- Alternative and International Cycles

FUSION SYNFUEL (HYDROGEN) PROJECT

A design study has been launched at LASL to assess the potential for economical production of hydrogen by thermochemical water-splitting using fusion-generated electricity and high-temperature process heat. The initial study focusses around hybrid thermochemical cycles that use a low-temperature electrolytic step. Emphasis was placed on the conceptual design and integration of a generalized fusion blanket with a specific thermochemical cycle.

The bismuth sulfate hybrid cycle was chosen for the initial phase of the study. The fusion blanket contained a mix of thermal energy; roughly two thirds of the energy was at an intermediate temperature of around 800 K and one third was available at 1500 K. Mass and energy balances and a preliminary design were completed for the study and reported earlier.(1)

The rationale for the use of a solid sulfate consists of the following:

- a. Precipitating an anhydrous sulfate from sulfuric acid solution may avoid corrosion problems associated with the handling of boiling sulfuric acid solutions. Materials selection may be simplified.

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- b. Heat penalties associated with the drying of sulfuric acid solutions to obtain a pure acid are also avoided. Efficiency improvement is a result.
- c. Lower acid concentrations may be used to precipitate solid sulfates; in principle, operation at these concentrations should lead to lowered electrical requirements in a hybrid cycle (thus raising the cycle's efficiency).
- d. Using a solid sulfate that decomposes near the maximum temperature of the heat source would lead to a poor thermal load matching. The use of bismuth sulfate that decomposes in steps at different temperatures simplifies the bad matching problem. The decomposition of SO_3 also occurs over a temperature range. It must be noted that the problems associated with solids handling at high temperature have not been completely identified and solved. Part of our future program includes the development of methods for manipulating and transferring heat to and from solid reactants and products.

Ideally, the sulfate should be insoluble in sulfuric acid solutions allowing for a relatively simple separation step such as filtration to be effected. Slight solubility may be tolerated provided that the metal cations do not interfere with the electrolytic process taking place in the cycle. The sulfate should preferably decompose to a solid oxide or an oxy-sulfate without the formation of a liquid phase.

We have considered soluble sulfates, for example, aluminum sulfate. They may have significant merit, however, solution drying and dehydration would be necessary.

Bismuth and antimony sulfates were initially chosen for investigation since they conform to some of the criteria. Bismuth sulfate decomposition is being pursued at this time. Published work indicates that bismuth sulfate decomposes with increasing temperature to sulfur trioxide and a series of oxide sulfates terminating in bismuth oxide.

Applying bismuth sulfate decomposition to the hybrid sulfuric acid cycle, we obtain the following steps:

1. $\text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 \text{ (aq.)} + \text{H}_2 \text{ (electrochem.)}$ 350 K
2. $\text{H}_2\text{SO}_4 \text{ (aq.)} + \text{Bi}_2\text{O}_3 = \text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3 + \text{H}_2\text{O}$ 350 K
3. $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3 = \text{Bi}_2\text{O}_3 + 3\text{SO}_3$ 1000 - 1500 K
4. $3\text{SO}_3 = 3\text{SO}_2 + 3/2\text{O}_2$ 1000 - 1500 K

In the design study mentioned above, the process was broken down into two portions: the low-temperature portion comprising the electrolyzer, the gas ($\text{SO}_3\text{-SO}_2$) separation train, and the bismuth sulfate precipitation vessel and a high-temperature portion comprising the decomposition reactors. The high-temperature portion of the design incorporated a series of three "falling-bed" reactors. A novel feature in their design was the projected solids heating system. Heating of the solid would be accomplished by direct thermal contact with the gaseous $\text{SO}_3\text{-SO}_2\text{-O}_2$ decomposition products that were heated in the main process heat exchanger operating at 1500 K. By means of this "chemical heat pipe" scheme, the heat of reaction would be absorbed by the bismuth sulfate as some of the SO_2 and O_2 partially reconverted to SO_3 . The circulation of large amounts of gases, in which only the sensible heat is transferred, would be avoided.

The thermal efficiency of the cycle, assuming a modest (30%) heat-to-work conversion, came out to 41%. Further iterations are being done on the cycle to achieve an efficiency of 50% or greater. An iteration of interest is the decomposition of $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ to $\text{Bi}_2\text{O}_3 + 2\text{SO}_3$. The $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ can be precipitated from sulfuric acid solutions of concentrations less than 1 M. Low acid concentrations will, in principle, permit lower voltages in the electrochemical step, minimize the work (electricity) requirement for the cycle, and thus raise its overall efficiency. A preliminary calculation indicates an achievable efficiency of 50% for this variation in the bismuth sulfate cycle.

EXPERIMENTAL RESEARCH IN SUPPORT OF DOE FUNDED CYCLES

Laboratory work is being carried out at LASL to determine the thermodynamics and kinetics of the total bismuth sulfate decomposition scheme. Some details of recent work are given below.

Experimental study has determined a sulfur trioxide partial pressure of 1 atm. at 876 K and a value for $\Delta H^\circ = +161$ kJ/mol for the $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3 = \text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ dissociation. Encouraging results on the rate of decomposition of $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ have been obtained by deliberately overheating samples of the sulfate 40-50°C higher than the final temperature. Pressure rose to the equilibrium value in times of 3-4 minutes, possibly due to an increase in heat transfer rate to the solid sample. Work is progressing on the second stage of sulfur trioxide evolution, $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3 = \text{Bi}_2\text{O}_3 \cdot \text{SO}_3 + \text{SO}_3$, at higher temperatures.

The rate of reaction of Bi_2O_3 with 1 M H_2SO_4 to form $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ was determined at 25 C by a calorimetric method. The reaction was complete in ~ 1.5 minutes. An analysis of the experiment gave a $\Delta H = -75.3$ kJ for the reaction. From this, the heat of formation of $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ was derived as ~ -1900 kJ.

ELECTROLYSIS OF HYDROGEN IODIDE SOLUTION

The study of the electrolysis of HI solutions as a possible hybrid step for the sulfuric acid-hydrogen iodide cycle (General Atomic) has continued. Experiments were conducted with 55% HI as the catholyte and a solution corresponding to saturated HI_5 as the anolyte. Using a platinized platinum cathode and a porous graphite anode and keeping the voltage below about one volt, short duration experiments have allowed the accumulation of reproducible data without serious problems of corrosion or plugging of the electrolyte circulation systems.

With Nafion membrane, cell potentials were found to increase substantially with increasing current density. A parasitic reaction occurs at low current densities. This was not thoroughly investigated. Observations have been made of the diffusion of iodine through the Nafion membrane. This may be the cause of this parasitic reaction which occurred regardless of whether platinized porous graphite or platinized platinum was used as the cathode. The cathode was strongly polarized with increasing current density while the anode remained quite stable. This was observed in all of the membrane electrolyses. Some experiments will be performed at temperatures where liquid iodine would be produced. If high overvoltages are again encountered, the study will be discontinued.

FUTURE EXPERIMENTAL WORK

Future work on solid sulfate decomposition includes obtaining the basic thermodynamic and kinetic data for the subsequent decomposition of $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ to lower oxide sulfates and eventually to bismuth oxide. These data will provide the necessary information for process design aimed at increasing the efficiency of the bismuth sulfate - hybrid sulfuric acid cycle. A bench-scale unit operating in a continuous mode will determine the important variables in the design of a solid sulfate decomposition reactor. Two heat transfer mechanisms are being evaluated for incorporation into this unit which will operate at a rate corresponding to the production of 2 liters/minute of hydrogen. The first mechanism will involve direct heating (radiation) as the sulfate is dropped through a "hot" tube. In the second mechanism, the "chemical heat pipe" proposed in the fusion synfuel design will be tested. SO_3 will be externally heated and the decomposition products, SO_2 and O_2 will be circulated past the incoming $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ solid, perhaps in a fluidized bed arrangement. Heat will be transferred to the solid partially by the absorption of chemical heat of reaction due to the recombination of SO_2 and O_2 and partially by cooling the circulating gas.

Eventually, we plan to utilize a solar furnace as a heat source for the solid decomposition facility.

I.E.A. AGREEMENT ON THERMOCHEMICAL HYDROGEN

An annual workshop on thermochemical and hybrid thermochemical-electrochemical processes for the production of hydrogen from water is a requirement

under Annex I of the IEA Implementing Agreement on Hydrogen. This year's workshop was held at the Euratom Joint Research Centre, Ispra, Italy immediately following the 2nd World Hydrogen Energy Conference in Zurich, Switzerland.

The next meeting of the Thermochemical Working Group (Annex I) is scheduled for September 1979 at the Los Alamos Scientific Laboratory.

CYCLE EVALUATION - ALTERNATIVE CYCLES

A preliminary examination of a magnesium-iodine cycle being investigated in Japan (2) is being conducted. The cycle consists of four steps and is similar in many respects to a calcium-iodine cycle reported earlier by the same authors.

Cycle efficiency for this type of cycle is not expected to be high since the necessity of drying solutions will use large amounts of low-temperature thermal energy. The cycle also includes the decomposition of HI and HI/I₂/H₂ separation. It is estimated that the efficiency for this cycle is less than 30%.

REFERENCES

1. L. A. Booth, M. G. Bowman, G. E. Cort, K. E. Cox, D. J. Dudziak, R. A. Krakowski, J. H. Pendergrass, and A. S. Tai, "Production of Electro-thermochemical Hydrogen Using a Fusion Source of High-Temperature Process Heat," proceedings 3rd American Nuclear Society Meeting on the Technology of Controlled Fusion, Santa Fe NM, May 1978.
2. W. Kondo, S. Mizuta, T. Kumagai, Y. Oosawa, and K. Fujii, "The Magnesium-Iodine Cycle for the Thermochemical Decomposition of Water," Vol. 2., pp. 909-922.

FACT SHEET

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Project Title: THERMOCHEMICAL PROCESS FOR HYDROGEN PRODUCTION

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Contract No.: W-7405-ENG-36 Effective Date: _____

Term of Contract: Continuing DOE Funding FY 78: \$250,000 (for Hydrogen)

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Goal: To develop an efficient and economical thermochemical cycle for the
production of hydrogen from water utilizing thermal energy sources
that become available.

Status: Continuing. 1) Experimental, a) Sulfate Decomposition b) Sulfate
Formation c) Hydrogen Iodide Electrolysis; 2) Fusion-Synfuel
Study (Hydrogen); 3) Evaluation of thermochemical Cycles; 4) IEA
Implementing Agreement.

Technical Monitor (if any): _____

Address: _____

Phone No.: _____

PROJECT: THERMOCHEMICAL PROCESS FOR HYDROGEN PRODUCTION

OBJECTIVE: DEVELOP EFFICIENT AND ECONOMICAL THERMOCHEMICAL CYCLE FOR THE PRODUCTION OF HYDROGEN FROM WATER

END ITEM: OPERATE AND TEST AT BENCH-LEVEL A CONTINUOUS CLOSED-CIRCUIT PROCESS. DEVELOP A SOLID DECOMPOSITION FACILITY AS THE FIRST UNIT. ASSESSMENT REPORT ON A FUSION-SYNFUEL (HYDROGEN) STUDY

RELATION TO
OVERALL PRO-

GRAM: SUPPORTS DEVELOPMENT OF THERMOCHEMICAL CYCLES SELECTED BY DOE/STOR

FUNDING

FY-77
\$220K

FY-78
\$250K

FY-79
\$250K